

Dissertation

**Removal of Polymer Coating with Supercritical
Carbon Dioxide**

Submitted by

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Abstract of Dissertation

Removal of Polymer Coatings with Supercritical Carbon Dioxide

This work investigates the use of supercritical fluids, and carbon dioxide in particular, for the removal of polymer coatings. Research into new supercritical fluid applications is nearly always based on a trial and error approach, and frequently requires evaluating each operation on a case-by-case basis. A significant improvement in this approach is accomplished with the development of a framework in which polymer-CO₂ interactions can be evaluated and the number of experimental trials reduced.

The basic model developed is built upon the three-component solubility parameter (HSP) concept, which is widely used in the coatings industry to aid in the selection of solvents. Temperature and pressure dependent HSP values have been developed for supercritical CO₂, using a methodology extendable to other supercritical fluids. Equations were also developed to calculate HSP's for cosolvents and polymers. With the solvent, cosolvent, and polymer thus fully characterized in terms of the HSP values, the systems are then analyzed in terms of the like and unlike (solvent/polymer, cosolvent/polymer, and solvent/cosolvent) binary pairs. In addition to this study, consideration of specific interactions, such as Lewis acid/base interactions between the solvent and polymer or between the cosolvent and polymer are examined for their role in determining a favorable (polymer coating removal) result.

The model was tested on two real-world applications: involving poly(methyl methacrylate) (PMMA) and polycarbonate (PC) coatings. Several organic liquids were evaluated as cosolvents, including at least one example of a non-polar fluid, a Lewis acid, and a Lewis base. Results of this study found the following interactions, listed in order of importance in the removal of polymer coatings, to be (1) specific interactions between the solvent and polymer, in the case of PMMA and CO₂, or specific interactions between the cosolvent and polymer, in the case of PC and CO₂, (2) weaken polymer/polymer interactions as a result of polymer swelling and subsequent lowering of the polymer HSP values, (3) specific interactions between the solvent and cosolvent are not necessary and in the case of specific interactions between the cosolvent and polymer, may be undesirable.

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.....*“I hear and I forget, I see and I remember, I do and I understand.”*

Confucius

To Jim Rubin, for taking the trip with me and making the journey worthwhile.....

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List of Symbols

T	Temperature
T_c	Critical temperature
T_r	Reduced temperature, T/T_c
T_{br}	Reduced boiling temperature, T_b/T_c
T_g	Glass transition temperature
P	Pressure
P_c	Critical pressure
P_r	Reduced pressure, P/P_c
V	Volume
ρ	Density
ρ_r	Reduced density, ρ/ρ_c
α^p	Polarizability
\mathbf{m}	Dipole moment
I	Ionization potential
\mathbf{s}	Collision diameter
r	Distance between molecules
r_o	Equilibrium distance between molecules
Q	Quadrupole moment
U	Total energy of a system
${}_1Q_2$	Heat transferred to a system
${}_1W_2$	Work transferred to a system
E	Internal energy
n	Ratio, $\left(\text{Internal Pressure} / \text{Cohesive energy density} \right)$
S	Entropy

H	Enthalpy
G	Gibbs free energy
d	Total solubility parameter
d_l	Solubility parameter – nonpolar component
d_t	Solubility parameter – polar component
d_d	Solubility parameter – dispersion component
d_p	Solubility parameter – polar component
d_h	Solubility parameter – hydrogen bonding component
x	Mole fraction
f	Volume fraction
R_o	Interaction radius
R_a	Distance (expressed as a radius) between two different HSP points
R_o^{liq}	Interaction radius based on polymer dissolution behavior in liquid solvents
R_o^{SCF}	Interaction radius based on polymer behavior in SCF
n_D	Index of refraction
ϵ	Dielectric constant
α	Thermal expansion coefficient
β	Isothermal compressibility
p_s	Saturation vapor pressure
$B(T)$	Tait parameters
B_o	Material dependent parameter
B_1	Material dependent parameter
A_o	Material dependent parameter
A_1	Material dependent parameter
A_2	Material dependent parameter
γ	Surface tension
P_s	Parachor parameter
k_D	Henry's law constant